

# CATALYTIC DEHYDROGENATION OF HYDROCARBONS: ALTERNATIVE, ONE STEP PROCESS TO PRODUCE PURE HYDROGEN AND CARBON NANOTUBE BYPRODUCTS

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## Introduction

Traditionally, hydrogen has been produced by reforming of natural gas to produce synthesis gas, followed by the water-gas shift reaction to convert CO to CO<sub>2</sub> and produce more hydrogen, followed by separation and purification procedures. In the "FutureGen" concept<sup>1</sup> advocated by the U.S. Department of Energy, the syngas would be produced by coal gasification.

Non-oxidative, catalytic decomposition of hydrocarbons is an alternative, one-step process to produce pure hydrogen. Nanoscale, binary Fe-based alloy catalysts supported on high surface area alumina [(0.5%M-4.5%Fe)/Al<sub>2</sub>O<sub>3</sub>, M=Mo, Ni or Pd] have been shown to have high activity for the catalytic decomposition of undiluted methane, ethane, or propane into pure hydrogen and multiwalled carbon nanotubes<sup>2,3,4</sup>. One of the problems with non-oxidative dehydrogenation is coking of the catalyst and reactor due to carbon build up. Under proper reaction conditions, however, these binary catalysts promote the growth of carbon nanotubes that transport carbon away from the catalyst surfaces, thereby preventing catalyst deactivation by coking as well as producing a potentially valuable by-product.

For utilization of fuel cells in vehicles, it is desirable to have a simple process for producing hydrogen from liquid fuels on-board. Therefore, we have also developed catalysts that are very effective for one-step production of pure hydrogen from cyclohexane and methyl cyclohexane<sup>5</sup>.

## Experimental Procedures

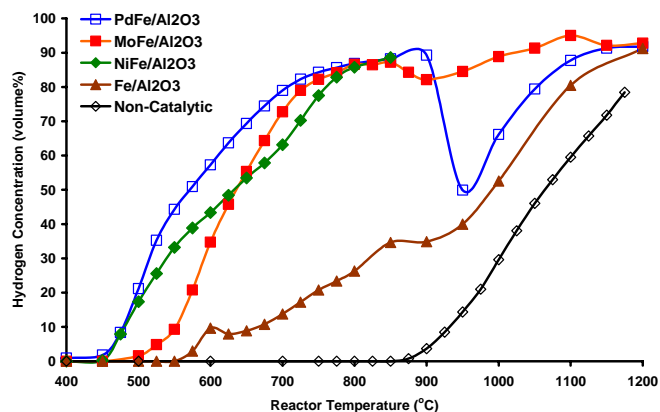
Detailed descriptions of the experimental procedures have been given elsewhere<sup>2,4,5,6</sup>. Briefly, the catalysts are prepared by deposition of the metal precursors onto the alumina or stacked-cone CNT by either coprecipitation or incipient wetness procedures using aqueous solutions of the appropriate metal salts. The resulting paste is extruded into pellets that are vacuum-dried and calcined for 5 hours at 500°C. Normally, one gram of catalysts is loaded in the continuous flow reactor and reacted in situ in flowing hydrogen at 700°C for 2 hours prior to reaction. The undiluted hydrocarbons are then fed to the reactor in precisely controlled amounts using mass flow controllers for gaseous alkanes and a syringe pump for liquid hydrocarbons. The products are measured by on-line gas chromatography.

## Results and Discussion

**Gaseous alkanes.** Nanoscale, binary, Fe-M catalysts supported on alumina (0.5%M-4.5%Fe/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, M = Ni, Mo, or Pd) have been shown to decrease the decomposition temperature of methane, ethane, and propane by 400-500 °C. For methane (Figure 1), the only decomposition products are hydrogen and carbon in the form of multi-walled carbon nanotubes (CNT), while ethane and propane decompose to hydrogen, methane, and CNT. The most active temperature range for all three feed gases is 650-800 °C, where 70-90 % of the product gas is pure hydrogen and the remainder is unreacted methane. In Figure 1, the hydrogen production from methane is shown as a function of temperature for the three binary

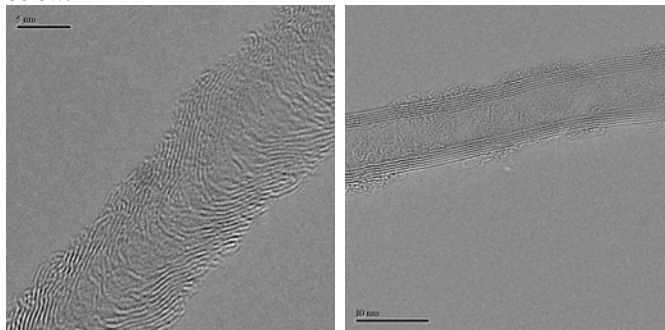
catalysts, a 5% Fe/Al<sub>2</sub>O<sub>3</sub> catalyst and the alumina support (non-catalytic).

Characterization of the catalysts by XAFS and Mössbauer spectroscopy, TEM, and XRD indicates that the active phase is an Fe-M-C austenitic metal alloy and that the catalyst particles are anchored to the alumina support by an Fe-aluminate, hercynite<sup>6</sup>. The catalysts exhibit good time on stream behavior because the Fe-M-C phases are very effective in stabilizing carbon in the form of CNT, which efficiently carry the carbon away from the active alloy particle surfaces.



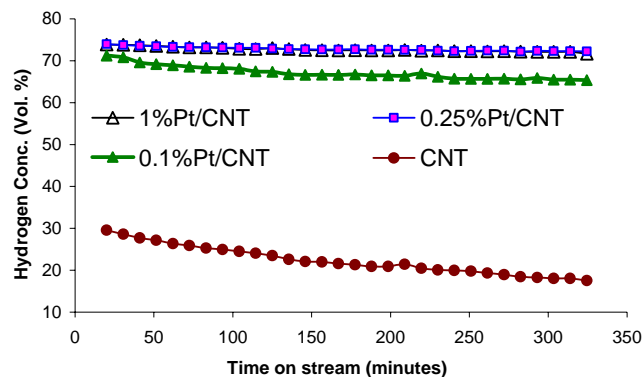
**Figure 1.** Catalytic decomposition of methane: hydrogen concentration vs. temperature

High resolution TEM has been used to investigate the structures of the CNT. Multi-walled CNT with parallel, concentric, graphene walls are produced at high temperatures (650-700 °C). At low temperatures (450-500 °C), a stacked-cone CNT (SCCNT) structure is produced in which the graphene sheets lie at an angle to the tube axis, which results in extensive graphene sheet edge openings at the circumference of the CNT (Figure 2). Consequently, most of the graphene sheet surface, both exterior and interior, is accessible from the outer periphery of the SC-CNT. Additionally, the outer surface of the SC-CNT has a high density of active carbene sites<sup>7</sup>. Because of this structure, the SC-CNT appear promising as hydrogen storage materials, catalyst supports, and sorbents. Preliminary measurements on hydrogen storage have been conducted by Bockrath and co-workers at the National Energy Technology Laboratory<sup>8</sup>. We have explored the use of SC-CNT as catalyst supports, as discussed further below.



**Figure 2.** Catalytic decomposition of propane produced stacked-cone CNT at 475 °C and multi-walled CNT with concentric parallel graphene sheets at 625 °C.

**Liquid hydrocarbons.** In our initial studies of catalytic dehydrogenation of liquid hydrocarbons, we are investigating dehydrogenation of the model compounds cyclohexane and methyl cyclohexane. Cyclohexane is completely converted to benzene and hydrogen at 315 °C using a catalyst consisting of only 0.25 wt.% Pt supported on stacked-cone CNT (Figure 3). Similar results were obtained for the catalytic dehydrogenation of methyl cyclohexane to toluene and hydrogen. Additional studies are planned using several alloy catalysts and other hydrocarbon liquids, including Fischer-Tropsch fuels.



**Figure 3.** Hydrogen production by catalytic dehydrogenation of cyclohexane using Pt on SC-CNT catalysts. The results obtained using the SC-CNT alone are also shown.

#### Future work

Topics to be investigated in future research are briefly summarized below.

1. Development of a fluid bed process for continuous production of hydrogen and carbon nanotubes by catalytic dehydrogenation of gaseous alkanes.
2. Further investigation of applications for stacked-cone CNT, including gas storage, catalyst supports, and as environmental sorbents.
3. Development of more economical alloy catalysts for dehydrogenation of hydrocarbon liquids.
4. Catalytic dehydrogenation of additional hydrocarbon liquids, including Fischer-Tropsch fuels.
5. Carry out an economic and energy balance analysis of catalytic dehydrogenation of gaseous and liquid hydrocarbon fuels.

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